

ANALYSES OF PRODUCTS FROM AUTOCLAVE REACTIONS: DERIVATION OF REACTION PARAMETERS

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Keywords: Hydrocracking, Decalins, Faujasites

ABSTRACT

This work presents energetics for high pressure hydroprocessing reactions derived from post analyses of liquid and gaseous products. Specifically, GC and GC/MS were used to follow the product distribution from the hydrocracking of methyldecalins over zeolite supported palladium and platinum catalysts as a function of temperature. Plain Arrhenius plots summarize key results and reveal possible connections in terms of 'activation energies' between hydrogen consumption and the amounts of different products. The total cycloalkane production and the consumption of hydrogen both show a simple temperature dependence with the same 'activation' energies. Methane production varies more rapidly with temperature but can still be described by a single exponential term. The final example, conversion to aromatics, displays a more complicated dependence with an accelerated yield at high temperature. This form of data analyses connects to a new routine for mass balance evaluations and it is now applied to model catalyst performance and to understand optimum reaction conditions. Other branches of this project include surface spectroscopic measurements of fresh, sulfided and used catalysts, characterization of partially hydrogenated naphthalenes and modeling of hydrogen activity at metal sulfides.

INTRODUCTION

The present work is twofold motivated. The overall project goal is to find optimum conditions for a two-stage conversion of polyaromatic feeds, modelled by 1-methylnaphthalene (1-MeNapht), to fuels [1]. The first step, hydrogenation to methyldecalins (MeDecs) is addressed elsewhere [2]. Within the above engineering framework several scientific challenges constitute a second motivation. One challenge is to improve mass-balance evaluations [3], another to identify surface intermediates by a combination of spectroscopic tools and quantum chemical calculations [4], and yet a third to derive energetics from product analyses. The present work addresses the third topic.

Conversion, product distribution and potential for commercialization were recently demonstrated for an optimized two-stage operation with an initial hydrogenation stage of 1-MeNapht to MeDecs over $\text{NiMo/TiO}_2\text{-Al}_2\text{O}_3$ and a second hydrocracking stage of MeDecs over Pd/Faujasite [5]. This work was extended with weight change measurements and physico-chemical characterization of surface sulfides formed by pretreatment in $\text{H}_2\text{S/H}_2$ and of carbonaceous residues formed during operation [6,7]. The extension represents an additional improvement over previous schemes for mass-balance evaluations based solely on analyses of liquid and gaseous phases.

MATERIALS AND METHODS

The catalysts were either prepared with surface impregnation techniques from aqueous solutions followed by calcination in air and sulfidation in $\text{H}_2\text{S/H}_2$ (400°C, 2h) or, for ion exchanged Faujasites, used as received from the manufacturer [5]. 1-MeNapht (98%, Aldrich) was used as received for the first reaction stage. The feed for the second stage, MeDecs, was synthesized with better than 95% selectivity [2]. The catalysts and feed were mixed (1:4 to 1:10) in a stirred batch autoclave, operated either as a closed or an open system under hydrogen (700-1500 psi). The liquid product was weighed and analyzed by GC/MS. The composition of the gaseous product was analyzed by GC. The mass of hydrocarbon gases was derived from the pressure change (closed systems) or from the volume of the gas product. The hydrogen amount was calculated from the pressure change before and after reaction (closed systems) or from the change in H:C ratio from feed to product (closed and open systems).

RESULTS AND DISCUSSION

The prime result is a novel compilation of performance data for a series of two-stage reactions of 1-methylnaphthalene conversion to gasoline components using different catalysts. These data clearly show the conversion and potential for an industrial process and the ratio between gaseous and liquid products [1,5].

The scientific results are exemplified by two figures showing the evolution of products as a function of temperature over Pt (Fig.1) and Pd (Fig.2) ion-exchanged Faujasites.

Figs.1 shows that the hydrogen consumption and the total production of cycloalkanes over Pt/Faujasite are well described by a single Arrhenius term with the same apparent activation energy, 30 kJ/mol. Methane production is again well described by a single exponential term but with a considerably larger 'activation energy' 150 kJ/mol. The conversion to aromatics displays a more complicated volcano shape vs. temperature and it is not meaningful to derive a single slope over the entire temperature range.

Hydrocracking of MeDecs over Pd/Faujasite (Fig.2) shows a similar behavior with the following 'activation energies': hydrogen consumption 29 kJ/mol, total cycloalkane production 27 kJ/mol and methane production 130 kJ/mol. Aromatics production again shows a more complex temperature dependence.

The simple temperature dependence of hydrogen consumption and cycloalkane production motivates the search for a simple reaction mechanism involving both functionalities. The apparent 'activation energy' is too low to be translated directly to a certain bond activation process and its origin from possibly counteracting enthalpy and entropy terms is not clear.

The mechanism is different for methane production with an 'activation energy' of 130-150 kJ/mol. This branch of hydrocracking resembles the hydrogenation of surface carbon in Fisher-Tropsch catalysis.

The separate temperature dependence of the aromatics production shows that these compounds are formed neither along the same route as methane nor the cycloalkanes. A bell curve is often the result of competing processes, in our case the onset of dehydrogenation and/or cleavage reactions.

CONCLUSIONS

Quantitative analyses of liquid products and off-gases from autoclave studies of hydrocracking of methyldecals over Pd/Faujasite and Pt/Faujasite catalysts are presented. The data shows that the mechanism for cycloalkane production is closely related to the hydrogen activity i.e. most likely to the generation of adsorbed atomic hydrogen. It also shows that the route for methane production is separate from this mechanism as well as from the path leading to aromatic compounds.

ACKNOWLEDGEMENTS

We acknowledge collaborations with P.Nordlander at Rice and D.W.Goodman at Texas A&M within the framework of this project. B.Demirel would also like to express her sincere gratefulness to W.D.Wiser, Univ.of Utah, for his help and kindness during most of this project.

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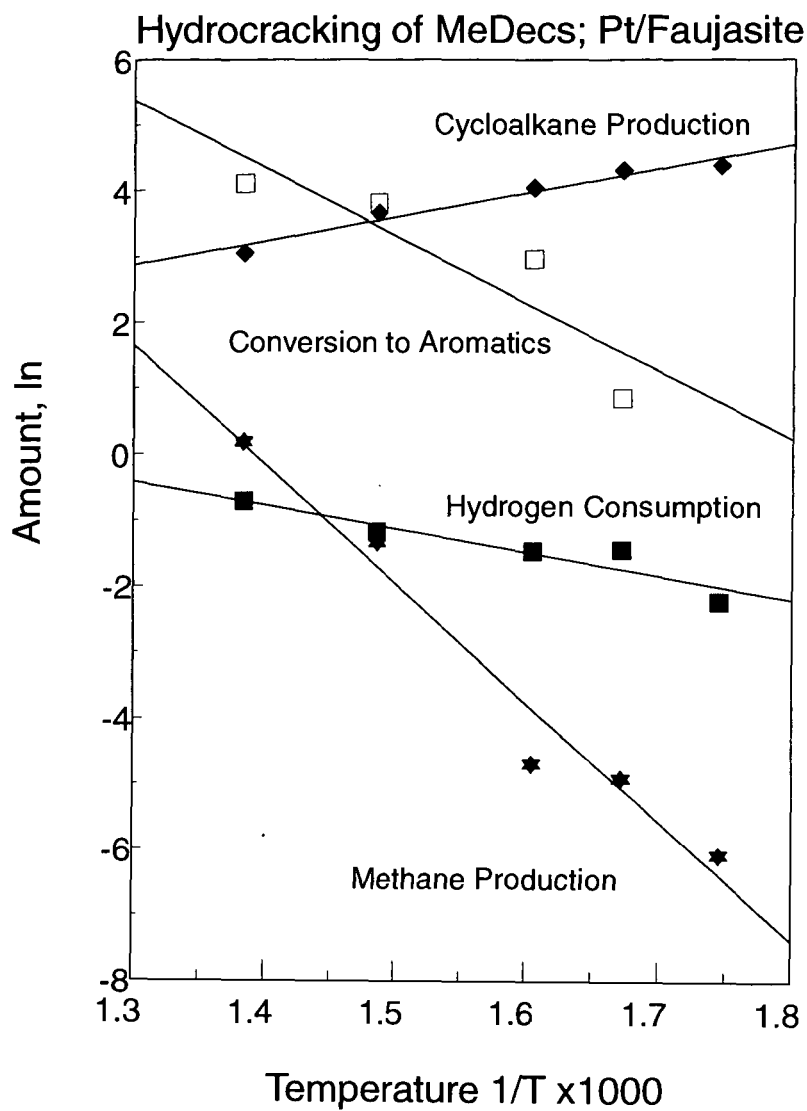


Figure 1.
Hydrocracking of Methyldecals over Pt/Faujasite. 700 psi. 1h. 10:1 Feed to Catalyst Ratio.

Hydrocracking of MeDecs; Pd/Faujasite

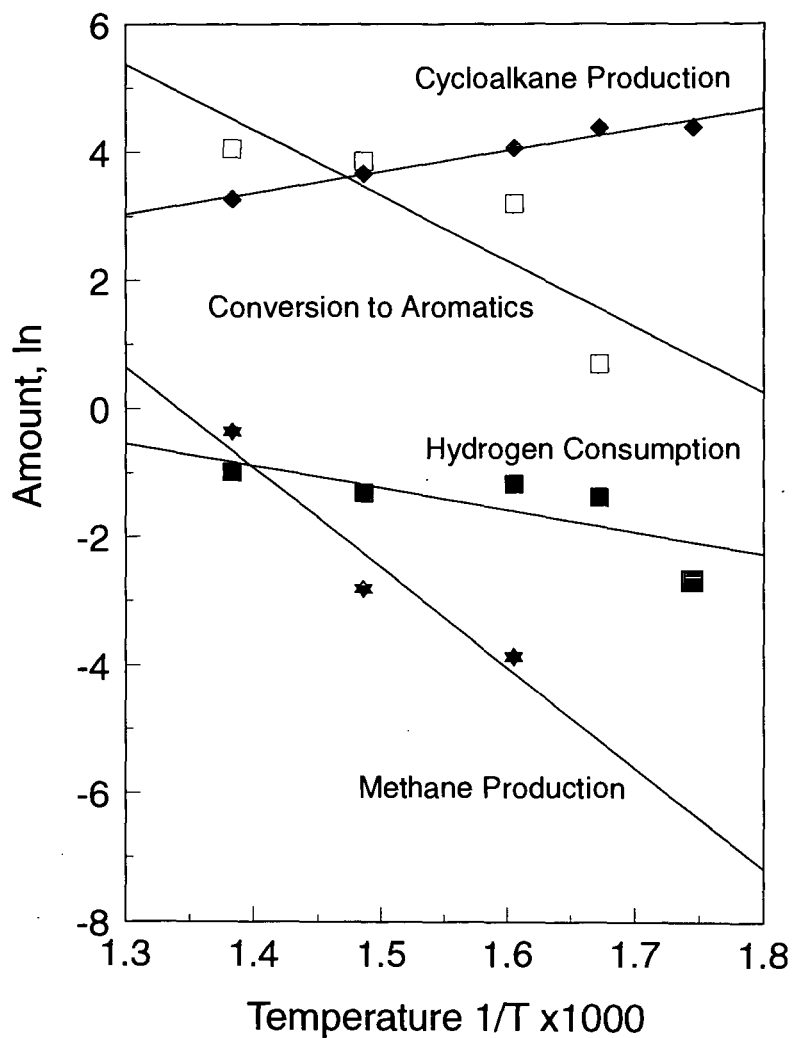


Figure 2.
Hydrocracking of Methyldecals over Pd/Faujasite. 700 psi. 1h. 10:1 Feed to Catalyst Ratio.